Reactive Transport Modelling of the contaminant release from Uranium Tailings using PhreeqC/Excel-coupling

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Abstract

Between the early 1950's and 1990, uranium mining and processing produced large quantities of radioactive mill tailings in Eastern Germany. Presently, the tailings sites are remediated according to the strategy of dry in-situ stabilization. Due to recontouring of the tailings, pore water is squeezed out resulting in a significant contaminant release. A multi-layer type soil cover will finally minimize the water infiltration, gas transport and seepage in the future.

The release of contaminated seepage water into ground and surface waters cannot be completely avoided due to lack of base sealing. For planing and monitoring of the remediation works geochemical models are essential in order to evaluate the long-term development of the contaminant release and to forecast future challenges for the water management and treatment at the site. In fact, the geochemical conditions within the tailings are highly complex due to the history of processing and discharge regime which resulted in a large heterogeneity of hydraulic and geochemical properties within the tailings impoundments.

This paper summarizes the current state of the development of a geochemical transport model in order to identify the geochemical processes responsible for the contaminant release in seepage water based on available lab-test data. For this purpose a 1-dimensional multi-component transport model was developed using the hydro-geochemical transport code PhreeqC and the spreadsheet program Microsoft Excel®. The coupling was realized using a Microsoft COM (component object model) enabling the simple manipulation of the PhreeqC input via Visual Basic for Applications (VBA) macro. Two infiltrative column experiments with tailings material from the tailings management facility (TMF) Culmitzsch (Seelingstädt) were used to validate the model approach by computing the effluent water composition of the columns.

Key words: uranium tailings, transport modeling, PhreeqC, column experiments, oxygen diffusion

Introduction

In 1990, the uranium production of SDAG Wismut in Eastern Germany was stopped. 45 years of uranium mining left behind legacies of ore mining and milling. Between 1960 and 1990, ores extracted in the Thuringian mining district were hydrometallurgically processed in the uranium processing facility at Seelingstädt. The tailings were disposed in the former open pits of Trünzig and Culmitzsch. In the course of the remediation of the tailings management facilities (TMF) at the Seelingstädt site a dry in-situ stabilization of the about 100 Mm³ tailings material is underway. An essential part of this remediation strategy refers to the catchment and treatment of contaminated pore and seepage water, which also represents a precondition for the geotechnical stabilization.

For planning and monitoring of the remediation activities geochemical models are necessary. They are used to understand the complex geochemical processes within the tailings body and to forecast the long-term development of contaminant release from TMF seepage water and thus the necessity of water catchment and treatment.

The structure of the tailings ponds is very complex resulting in heterogeneous hydraulic properties based on the tailings discharge technology. Moreover, various geochemical processes interact with each other depending on the small-scale variations of the environmental conditions. Several 2D/3D reactive transport models have already been developed on behalf of WISMUT. However, their complexity limits the detailed understanding of single processes responsible for the contaminant

release. Therefore, the applied model should be kept as simple as possible with the main focus on the geochemical processes while reducing the description of hydraulic conditions to the essential aspects.

Thus, a simple 1-dimensional geochemical transport model was developed to describe the contaminant release and transport in the vadose zone of the tailings material. The model implementation comprises the coupling of the hydrochemical transport code PhreeqC (Parkhurst and Appelo, 1999) with the spreadsheet program Microsoft Excel®. In order to calibrate this model approach, data from infiltrative column experiments in the laboratory were used. With these experiments, processes of the long-term contaminant release from tailings material of the TMF Culmitzsch were examined.

Site characterization

The TMF Culmitzsch comprises two tailings ponds A and B occupying 158.1 ha and 75.8 ha, respectively (Fig. 1). The total volume of the tailings amounts to 61.3 Mm³ for pond A and 23.6 Mm³ for pond B with corresponding maximum thicknesses of 72 m and 68 m.

Figure 1 *Tailings management facility (TMF) Culmitzsch, Seelingstädt, Germany (November 2015).*

The discharge of tailings from the uranium processing facility Seelingstädt into the TMF started in 1967, immediately after termination of the uranium ore mining in the Culmitzsch open-pit. The dam structures were already constructed during the ongoing open-pit mining operation before tailings discharge.

Tailings pond A was filled with silicate tailings from the sulfuric acid ore processing via annular discharge pipes. The discharge was accomplished from certain points along the pipes both into the pond interior as well as in direction of the south/southeast dam. Due to a changing discharge regime and the relocation of the discharge points during the operation period, a strong lateral and vertical differentiation in soil-physical and structural composition of the disposed tailings resulted over time.

In the tailings pond B, the residues of soda-alkaline uranium ore leaching were disposed. Later on in the operation period, lime mud from the water treatment was disposed in the northern part of pond B. The discharge of tailings was finished in 1991.

Since 1991, remediation activities have been conducted at the TMF Culmitzsch with the aim of dry in-situ stabilization of the entire impoundment. The applied remediation technology comprises an interim cover, geotechnical stabilization as well as contouring and covering of the facility with material from nearby mine dumps. Contaminated pore water and seepage water is collected and treated.

Methodology of model development

Experimental data basis

Two column experiments were conducted for the duration of roughly one year using tailings material from drillings in tailings pond A (CA68) and pond B (CB36-8). Mixed material from different depths was filled in PVC tubes (40 cm high, 19 cm in diameter) and compacted in layers. Once a week, the

columns were irrigated on the top with 0.5 l infiltration water (CA68: distilled water, CB36-8: seepage water from dump material used for contouring of the TMF Culmitzsch) over a period of 24 h. Bulk samples of the column effluents were analyzed every two weeks. The experiments were conducted at room temperature, and the columns remained open in contact with the atmosphere in order to assess the effects of oxygen diffusion on geochemical reactions in the tailings material. With an initial water saturation of 36.7 % the tailings of column CA68 were unsaturated whereas column CB36-8 showed almost saturated conditions. In the latter case, a residual gas proportion of 2 % of the total porosity was assumed for modelling. Table 1 summarizes the main soil physical parameters of both column experiments.

Table 1 Soil physical parameters of the column experiments CA 68 and CB 36-8.

Parameter	Units	CA 68	CB 36-8
Material level in column	cm	38.5	31.0
Soil type (German class.)	-	Ss	Su3
Density (wet)	g/cm³	1.554	2.118
Density (dry)	g/cm³	1.374	1.762
Initial water saturation	-	0.367	0.98
Total porosity	%	49.1	35.6
Gas phase	%	31.1	0.7
Mobile water	%	9.2	17.4
Adhesive water	%	8.8	17.5
Immobile water	%	6.6	14.0
Dead water	%	2.4	3.5
Duration of experiment	days	336	315
Infiltration water	-	Distilled water	Dump seepage water
Mean drainage	l/week	0.447	0.490
Permeability	m/s	2.03E-07	2.76E-07

Solid samples of the tailings underwent full geochemical analyses using ICP-OES and XRD in order to determine the initial mineral phase assemblage (Tab. 2).

Table 2 Mineral phase assemblage calculated from geochemical analyzes and identified by [a]XRD.

Mineral phase	CA68 [ppm]	CB36-8 [ppm]	Mineral phase	CA68 [ppm]	CB36-8 [ppm]
Albite [a]	10 000	10 000	Magnetite [a]	10 000	-
Anorthite [a]	10 000	10 000	Manganite	213	619.8
Barite	143	565.9	Millerite	60.0	229.3
Calcite *	40 096	60 753	Pyrite *	12 332	618
Chalcopyrite	367	-	Pyrolusite	105	306.4
Chlorite [a]	40 000	70 000	Quartz [a]	500 000	370 000
Dolomite *	9 033	110 641	Rhodochrosite	278	810
Galena	31	-	Siderite *	21 698	52 581
Gibbsite	11 828	22 900	Smithsonite	41	-
Greenockite	0.8	-	Sphalerite	144	-
Gypsum	14 089	39 889	Strontianite	71	164.4
Iron hydroxide (amorph.)	17 000	28 417	Uraninite	29.6	35.4
Kaolinite [a]	20 000	20 000			

*kinetic approach

The column effluent immediately collected after the first irrigation step is assumed to represent the initial pore water composition in the tailings material. Before modelling, the chemical composition of the initial pore water was balanced out using PHREEQC (Tab. 3).

Table 3 *Initial aqueous species concentrations in the tailings pore water and infiltration water (IW) [mg/l].*

Species	CA68	CB36-8	IW*	Species	CA68	CB36-8	IW*
Temp [°C]	22	-	-	As	0.068	0.220	0.005
pH	8.2	8.4	7.85	Ba	0.026	0.029	0.031
Eh [mV]	370	440	525	Cd	0.002	0.002	0.001
$O_{2(aq)}$	7.03	9.20	8.77	Cu	0.035	0.027	0.020
Na	4 290	5 656	14	Fe	0.10	0.039	0.070
Mg	1 235	549	120	Mn	14.17	0.632	0.681
K	126	129	3	Ni	1.04	1.215	0.020
Ca	445	461	180	Pb	0.02	0.020	0.020
SO_4	13 370	12 872	490	Si	5.30	3.864	3.203
Cl	1 121	1 379	16	Sr	6.05	5.336	0.187
HCO_3	243	648	543	U	4.34	12.973	0.550
Al	0.10	0.146	0.055	Zn	0.037	0.029	0.001

* Dump seepage water used for column experiment CB36-8

Conceptual model setup

The 1-dimensional geochemical transport model was created by coupling of the geochemical reaction code PhreeqC (Parkhurst and Appelo, 1999) and the spreadsheet program Microcsoft Excel® via a Microsoft COM (component object module). The PhreeqC input can be optionally adapted after each batch reaction by the help of a Visual Basic for Applications (VBA) macro (Charlton and Parkhurst, 2011).

Since PhreeqC alone is only suitable for modelling saturated flow or aqueous diffusion, it does not consider gas transport in unsaturated conditions. However, the gas phase composition especially in the column experiment CA68 is influenced by interactions with the liquid phase (i.e. HENRY-exchange, O_2 and CO_2 consumption or production by chemical reactions) as well as by gas transport. The latter one can be controlled by convection and/or diffusion. With respect to the grain size distribution of the tailings material, gas convection can be neglected in these column experiments. The O_2 and CO_2 replenishment by diffusion was computed in MS Excel according to FICK's law for each time step (batch reaction) and each model cell. The effective gas diffusion flux is calculated from the gradient between the gas concentration in the considered model cell (c_i) and the previous cell (c_{i-1}) taking also into account the simultaneous gas transport into the following cell (c_{i+1}) (Eq. 1).

$$q_{O2} = D_{eff} \cdot \frac{c_{i-1} - c_i - c_{i+1}}{\Delta x} \cdot \Delta t \qquad \text{(Equation 1)}$$

Thereby, D_{eff} is the effective diffusion coefficient, Δt is the time step of the batch reaction and Δx is the length of each model cell. The effective gas diffusion coefficient was set to 1E-06 m²/s for all model cells in accordance with Eckart et al. (2006). The resulting molar amount of O_2 (CO_2) in the gas phase of each model cell after the batch reaction and diffusion step is transferred from the Excel balance calculation into the PhreeqC input for the next reaction step using a VBA macro.

The residence time of the percolation water reproduced by the model is crucial for the contaminant release. In accordance with the conceptual approach in TENSIC (Eckart et al., 2006) or HYDRUS (Jacques et al., 2013) it is therefore assumed that the liquid phase is subdivided into a mobile and an immobile phase depending on the geotechnical properties of the tailings (Tab. 1). The immobile phase comprises the adhesive water, which entirely moisten the solid particle surface (Fig. 2). The dead water in isolated pores is assumed not to contribute to the contaminant release. The essential geochemical processes, as for example pyrite oxidation, mineral dissolution/precipitation, ion exchange and sorption, are assumed to take place in the immobile phase.
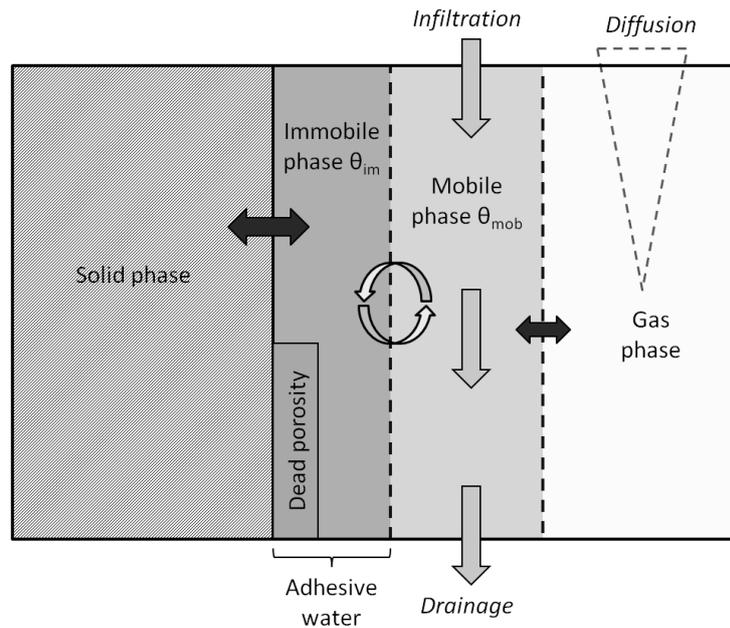
Figure 2 *Conceptual structure of a model cell with physical non-equilibrium (mobile-immobile water) transport.*

The mobile phase will be permanently exchanged by the input of infiltration water (Tab. 3). It represents the medium of solute transport in the strict sense. The mobile and the immobile phase stay in a mixing equilibrium. The mass exchange rate between both phases is given by their mixing ratio. Additionally, after each batch calculation a balance with the gas phase is enforced so that oxygen and carbon dioxide can be solved in or degassed from water according to HENRY's law.

For simplification, it was assumed that the gas volume in the unsaturated pore space of the tailings material is equal in all depth of the column and remains constant over time.

Both columns are discretised into three equally sized model cells (CA68: 12.8 cm; CB36-8: 10.3 cm). Initially, each model cell contains pore water with the chemical composition of the first effluent (Tab. 1) both in the mobile and the immobile phase.

The hydraulic transport is realized by shifting the water composition of the mobile phase from one to the next model cell after each reaction step (Fig. 2). The allocation of the mobile phase water composition is realized using the VBA script language in Excel.

The immobile water remains in each model cell and its composition is newly calculated after each reaction step (Fig. 2).

The time resolution (Δt) for a single reaction step depends on the permeability of the tailings material (k_f) and the effective porosity (n_{eff}) which is assumed to be equal to the proportion of the mobile water (Tab. 1).

$$\Delta t = \frac{n_{eff}}{k_f} \qquad\qquad \text{(Equation 2)}$$

Modelling results and discussion

The general flow conditions within the tailings columns could be well reproduced even by a simple hydraulic approach based on the geotechnical properties and physical non-equilibrium transport using a mobile-immobile model. The hydraulic calibration was performed by adjusting the mixing ratio between mobile and immobile phase to 0.4 in consideration of the volumetric ratios based on soil physical properties (Tab. 1) for both column experiments in order to fit the chloride release curve with the experimental data (Fig. 3). The geochemical data of the column experiments and the modelling results for pH- and redox (pe) conditions as well as for Na, Cl, Mg, Ca and SO₄ concentrations are compared in Figure 3. The concentrations of the columns' effluent could be fitted quite well by the

model calculations. However, uncertainties still exist with regard to the Mg release from the CA68 column.

The dissolution and/or precipitation of most minerals contained in the solid tailings assemblage was considered to occur under equilibrium conditions in contact with the immobile water phase (Tab. 2).

The oxidation of pyrite with oxygen is assumed to be kinetically controlled depending on the amount of oxygen diffusing within the unsaturated pore space into the column material. The specific oxidation rate for pyrite is considered within the PhreeqC database *wateq4f.dat* according to Williamson and Rimstidt (1994).

Despite ongoing dissolution of pore water by infiltrating water, the measured SO_4 concentrations reach a stable level of roughly 2000 mg/l in both columns which could be predominantly modelled by gypsum dissolution and less by pyrite oxidation (ca. 1400 mg/l in the model).

The model approach has shown that the adjustment of the calcite equilibrium is inhibited in the experiments. However, the kinetic calcite dissolution according to the mechanistic approach from (Plummer et al., 1978) did also not fit well because it is based on experiments on synthetic calcites. However, natural calcites which can be assumed to occur in the tailings material contain impurities which lead to sorption processes on the crystal surface. This, in turn, inhibits the calcite dissolution (Svensson and Dreybrodt, 1992). Thus, the kinetic for the calcite dissolution was implemented according to Chou et al. (1989).

In addition, it was found that also the Mg concentration strongly depends on the dissolution kinetic of dolomite. Another important factor controlling the HCO_3-content in the model simulation was found to be the kinetics of siderite.

Table 4 *Kinetic rates (r) for mineral dissolution and precipitation considered in the model.*

Mineral phase	Kinetic equation	Constants	Reference
Pyrite FeS_2	$r = 10^n \cdot m_{DO}^{k1} \cdot m_{H+}^{-k2}$ $[r] = \frac{mol}{m^2 \cdot s}; [m] = \frac{mol}{kg}$	$n = -8.19\,(\pm 0.10)$ $k_1 = 0.50\,(\pm 0.04)$ $k_2 = 0.11(\pm 0.01)$	Williamson and Rimstidt, 1994; Parkhurst and Appelo, 1999
Calcite $CaCO_3$	$r = k_1 \cdot a_{H+} + k_2 \cdot a_{H2CO3} + k_3 \cdot a_{H2O} - k_4 \cdot a_{Ca+2} \cdot a_{CO3-2}$ $[a_i] = mol/cm^3$	$k_1 = 8.9 \cdot 10^{-5}$ mol cm^{-2} s^{-1} $k_2 = 5.0 \cdot 10^{-8}$ mol cm^{-2} s^{-1} $k_3 = 6.5 \cdot 10^{-11}$ mol cm^{-2} s^{-1} $k_4 = 1.9 \cdot 10^{-2}$ mol cm^{-2} s^{-1}	Chou et al., 1989
Dolomite $(Ca,Mg)CO_3$	$r = k_1 \cdot a_{H+}{}^n + k_2 \cdot a_{H2CO3}{}^n + k_3$ $[a_i] = mol/cm^3$	$n = 0.75$ $k_1 = 2.6 \cdot 10^{-7}$ mol cm^{-2} s^{-1} $k_2 = 1.0 \cdot 10^{-8}$ mol cm^{-2} s^{-1} $k_3 = 2.2 \cdot 10^{-12}$ mol cm^{-2} s^{-1}	Chou et al., 1989
Siderite $FeCO_3$	$r = k_{H+} \cdot a_{H+}{}^n$ $[a_i] = mol/cm^3$ (pH = 2...4, T = 25°C)	$k_{H+} = 1.79 \cdot 10^{-8}$ mol/cm² s^{-1} $n = 0.75$	Golubev et al., 2009

Distinct differences between experimental data and model results occur for Mg in the column CA68. The measured concentrations slightly decrease, but do not reach zero. Hence, they do not represent a pure washout effect. Taking into account the kinetic of dolomite dissolution (Tab. 4) instead of equilibrium conditions resulted in better model results for CB36-8 compared to CA68. The still remaining difference between modelled and measured concentrations especially for CA68 might be caused by the input parameters for the mineral assemblage of the tailings which were deduced from geochemical analyses of the borehole material. The column material can show slight differences which might be sensitive to the model results.
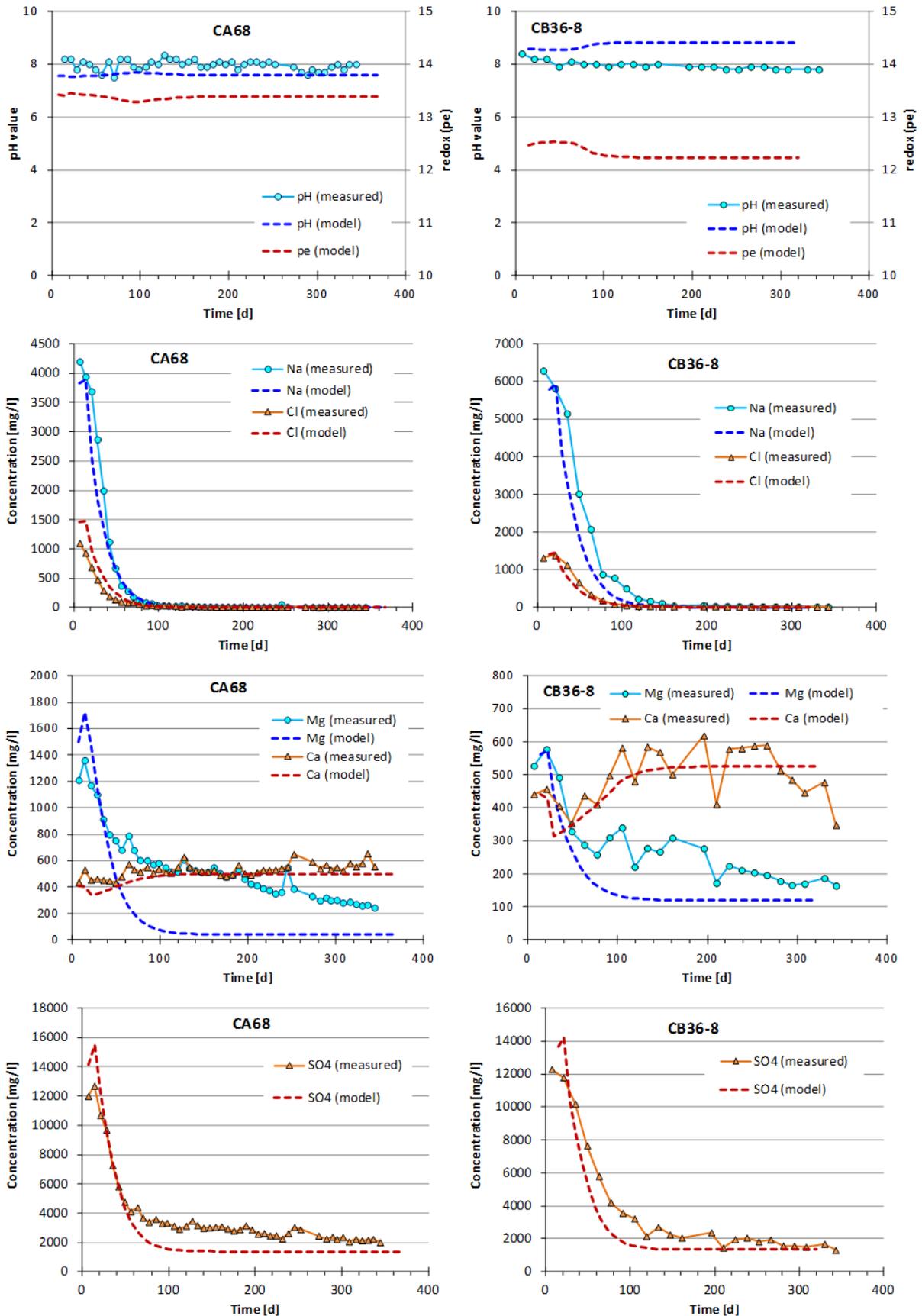
Figure 3 *Comparison of measured and modelled concentration developments of major constituents for the column experiments CA 68 (left) and CB 36-8 (right).*

Conclusions

The general model approach by coupling PhreeqC and MS Excel is appropriate to simulate the general geochemical processes and the 1-dimensional contaminant transport with consideration of gas transport by diffusion within tailings material of the TMF Culmitzsch.

At present, the major processes of mineral dissolution and precipitation under equilibrium or kinetic conditions are considered in the model. The geochemical milieu in the column experiments is strongly determined by gypsum equilibrium as well as the kinetic dissolution of carbonates (calcite, dolomite, siderite) and to less extent pyrite oxidation.

Next efforts will be undertaken to examine the sensitivity of the initial mineral assemblage and pore water composition with respect to the modelling results.

Future tasks will deal with the impact of sorption (e.g. on amorphous $Fe(OH)_3$ or $AlOOH$) and ion exchange reactions on trace metal concentrations in the effluent as well as the presence of organic matter (e.g. humic acids) on redox reactions in the column experiments. Furthermore, the formation of alkaline earth uranyl carbonate species (Bernhard et al., 2001) is supposed to influence the uranium speciation and thus its sorption and transport behaviour in the tailings material which needs verification, too.

Up-scaling of this 1-dimensional model approach to the field scale of the TMF Culmitzsch needs further efforts with regard to the extension of the current conceptual model as well as data acquisition for model parameterisation.

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